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Sorbent Selection for the CAFB Residual Oil Gasification Demonstration Plant

Westinghouse Research Labs, Pittsburgh, Pa

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SORBENT SELECTION FOR THE CAFB RESIDUAL OIL GASIFICATION DEMONSTRATION PLANT

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16. ABSTRACT The report gives results of evaluations of limestones from Texas and Mexico as candidate sulfur sorbents for the chemically active fluid-bed (CAFB) gasification demonstration plant at San Benito, Texas. Preliminary laboratory tests show that three limestones quarried in Texas and one quarried in Mexico should be suitable sorbents, based on availability, chemical characterization, physical characterization, attrition behavior, and chemical reactivity as sulfur sorbents. Current sorbent selection criteria are being refined.

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SECTION 1

INTRODUCTION

The CAFB (Chemically Active Fluid Bed) process is being developed under EPA sponsorship to retrofit electrical utility power plants to utilize high sulfur residual fuel oils or refinery bottoms. Coal is also being investigated as a fuel. In this process, the residual fuel oil is gasified by injecting it into an air-fluidized bed of lime operating at temperatures from 870-920°C, where the fuel sulfur is trapped in solid form, and the desulfurized hot gas (~ 870°C) is used to fire a steam boiler. The process has been developed in a 1 MW pilot plant by Esso at their Abingdon (England) Research Center.[1] Successive evaluations of the process by Westinghouse led to a demonstration plant design and cost estimate for a 50 MW demonstration plant.[2] Currently Foster-Wheeler are under contract to build a 16 MW_e retrofit CAFB unit for the San Benito (Texas) station of the Central Power and Light Co. A simplified illustration of the process concept is shown in Figure 1. The demonstration plant design incorporates a spent sorbent regenerator to air oxidize the calcium sulfide to sulfur dioxide and calcium oxide. The gas stream from the regenerator contains 6 to 10 percent by volume sulfur dioxide and is converted to elemental sulfur.

In support of the Westinghouse design, experimental tests were carried out to identify suitable limestones from the New England region for use in the process at a Providence Rhode Island site. A change in the demonstration plant site to San Benito mandated that limestones available in the Texas area be assessed for their suitability in the CAFB process.

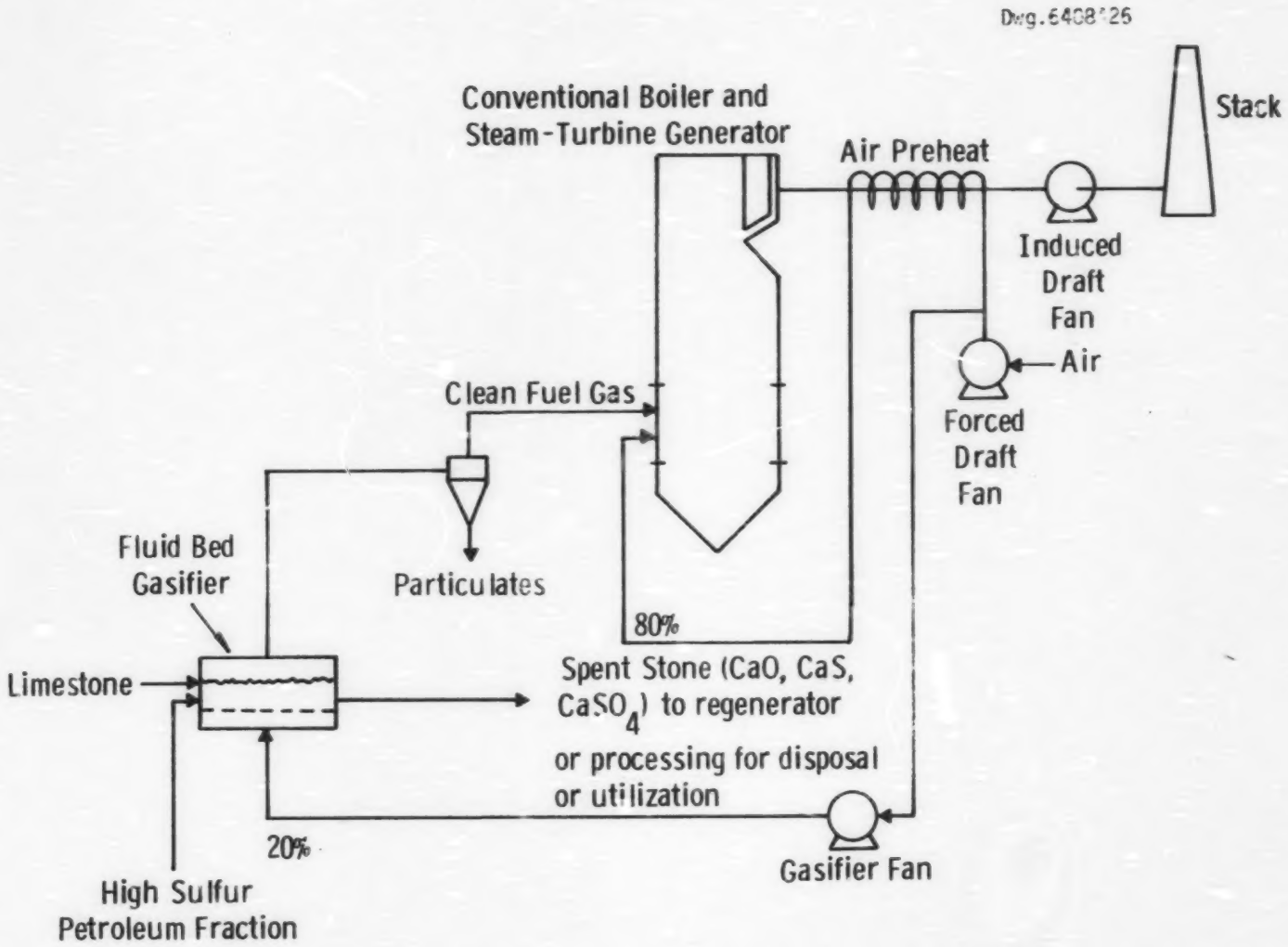

Fig. 1 — CAFB gasification power plant schematic

SECTION 2

CONCLUSIONS

Of the stones tested, the limestone from the Uvalde County mine of White's Mines, Inc. is the best choice for use at the San Benito plant. The stone from Parker Brothers is the second choice.

It is clear that the current test procedure did not lead to clear distinctions between most of the stones tested. The cost of the sorbents should therefore determine the choice of sorbent.

SECTION 3

RECOMMENDATIONS

1. Further investigations on these stones at the laboratory level should be pursued when further data describing operating experience on the Esso CAFB pilot plant become available. The principal questions which should be addressed are

(a) How much attrition occurs under reducing/sulfidation conditions.

(b) What is the reactivity of the sorbents after exposure to the regeneration process.

(c) Do these stones differ as to their suitability for the stone disposal process chosen for the San Benito plant.

2. Operating experience on the Esso plant, since 1973 with different sorbents should be reviewed, to develop superior sorbent selection tests.

3. Two other sources of calcium carbonate for the CAFB demonstration plant should be investigated: carbonates from marine sediments on the Gulf-coast, and industrial waste products containing calcium carbonate.

SECTION 4

SELECTION CRITERIA

Previous work by Westinghouse in evaluating processes which use calcium-based sorbents for high temperature desulfurization (i.e., in fluidized bed coal combustion, low Btu coal gasification, and CAFB gasification), led to the following general categories of criteria for selecting sorbents.[3,4]

- acceptor properties of the stone for sulfur removal
- attrition resistance of the stone
- trace and minor element emission characteristics
- regeneration characteristics
- suitability of spent sorbent for final processing for disposal
- economic availability of the stone

The development of rigid selection criteria based on the above categories is an evolutionary process. The variety of process options available in the desulfurization circuit of the gasification system require that a great deal of flexibility be built into the criteria. For example, fifteen process alternatives have been identified for disposal of the spent sorbent. It was not realistic to attempt an assessment of the impact of disposal processes on each candidate stone.

The procedure followed was to identify candidate stones using available literature and expertise on the limestone industry in the area surrounding San Benito. The attrition as measured by elutriation losses suffered by samples of these stones in a small fluidized bed unit under calcination conditions, was measured. The samples were evaluated for their reactivity to hydrogen sulfide in a fuel gas mixture at 871°C. Trace element analyses of the minerals were carried out.

ACCEPTOR PROPERTIES OF THE STONE FOR SULFUR REMOVAL

The standard test for sulfur removal is carried out by sulfiding limestone in a modified duPont thermogravimetric reactor using 0.5% H_2S/ fuel gas as reactant at 871°C. The stone particle size selected for testing was 1000-1200 micron diameter. Stones which have satisfactory desulfurization performance form 30% (molar) calcium sulfide within 7 to 8

minutes of exposure to the gas, (limestone 1359, Denbighshire limestone). The test may be regarded as a necessary, but not sufficient condition for adequate desulfurizing properties. All limestones tested to date have proven satisfactory sulfur acceptors in this test. It appeared from the most recently available test data from Abingdon, that in fact there is little difference in the intrinsic desulfurization performance of different stones.

ATTRITION

The attrition test is thought to give a reasonable guide to behavior in the Esso batch units. As reported previously,[3] Pfizer Adams calcite and Conklin limestone showed high attrition losses in our tests, and were rejected by Esso for the same reason on the basis of their own tests. Aragonite and limestone 1359 suffered low attrition losses on their unit and in the Westinghouse test and were thought suitable as sulfur sorbents.

Denbighshire limestone had an intermediate type of behavior on the Exxon unit: in calcination its elutriation losses were high relative to limestone 1359, in agreement with the Westinghouse attrition test. However, on sulfidation/regeneration cycling it had the lowest attrition rate of stones tested.

The current procedure is to accept sorbents with attrition losses of $\sim$ 2%, reject those with attrition losses of $\sim$ 10%, and take no decision based on attrition in the case of stones with intermediate attrition behavior.

GRAIN SIZE

Currently, it is believed that massive-grained sorbents such as Pfizer Adams, or Canaan dolomite are subject to heavy attrition when fully calcined. It is also thought that extremely fine-grained sorbents are also prone to attrition. Satisfactory performance is expected from stones in the range [5-250] micron grain size.

TRACE ELEMENTS

Trace elements are of significance only in that they might contribute to overall plant emissions. None of the elements considered to be of vital environmental concern are found at high levels in limestones. The atomic emission analyses carried out are essentially a check to see if the normal pattern of trace metals is found in any given limestone.

SECTION 5

CANDIDATE SORBENTS

LIMESTONE DEPOSITS IN TEXAS AND MEXICO

Abundant surface outcrops of limestone are prevalent in Texas which vary in the chemical composition and the physical properties of the stone. High-calcium limestone is quarried in a restricted zone within the Lower Cretaceous age, outcropping in a narrow 250 mile area west of the city of Waco, extending through Austin, north to San Antonio to Del Rio (Fig. 2). Major limestone producing counties (Val Verde, Edwards, Kinney, Real Counties) lie in the southern regions of the Edwards Plateau adjacent to the boundary demarcating central Texas from the neighboring coastal Plain area.

These lower Cretaceous limestones include a variety of stone compositions ranging from soft argillaceous stones relatively high in clay impurities to hard massive limestones generally high in the content of calcium carbonate. The hard, thick-bedded and massive limestones of the Edwards and Devils river formations are exceptionally pure. The Report of Investigations #56 of the Bureau of Economic Geology indicates that the average $CaCO_3$ content of the lower Cretaceous limestones is 98%, with 47% containing 97 + % $CaCO_3$. [With regard to the $MgCO_3$ content, less than 10% were completely free of magnesium as detected by flame photometry analysis, roughly 40% contained < 1% $MgCO_3$, and approximately 70% of the total samples contained < 3% $MgCO_3$. The non-carbonate composition of the lower Cretaceous limestones from the Edwards Formation had been analyzed].

In the Gulf Coastal Plains of Texas, limestone deposits contribute < 5% to the carbonate industry and outcrop as minor occurrences of thin beds of impure Tertiary stone. The local deposits are commonly associated with salt domes and Quaternary caliche, interbedded with large deposits of unconsolidated sands and clays. The Gulf Coastal Plains region, therefore, is an area generally lacking in carbonate material resources with the exception of its extensive oyster shell production. Two stone producers quarry in Calhoun and Matagordo Counties (170-220 miles from San Benito, Texas).

The limestone in Mexico is categorized on the basis of purity and physical characteristics as either marl, marble, metamorphic limestone or calcite. The stone is chiefly calcium carbonate with minor trace

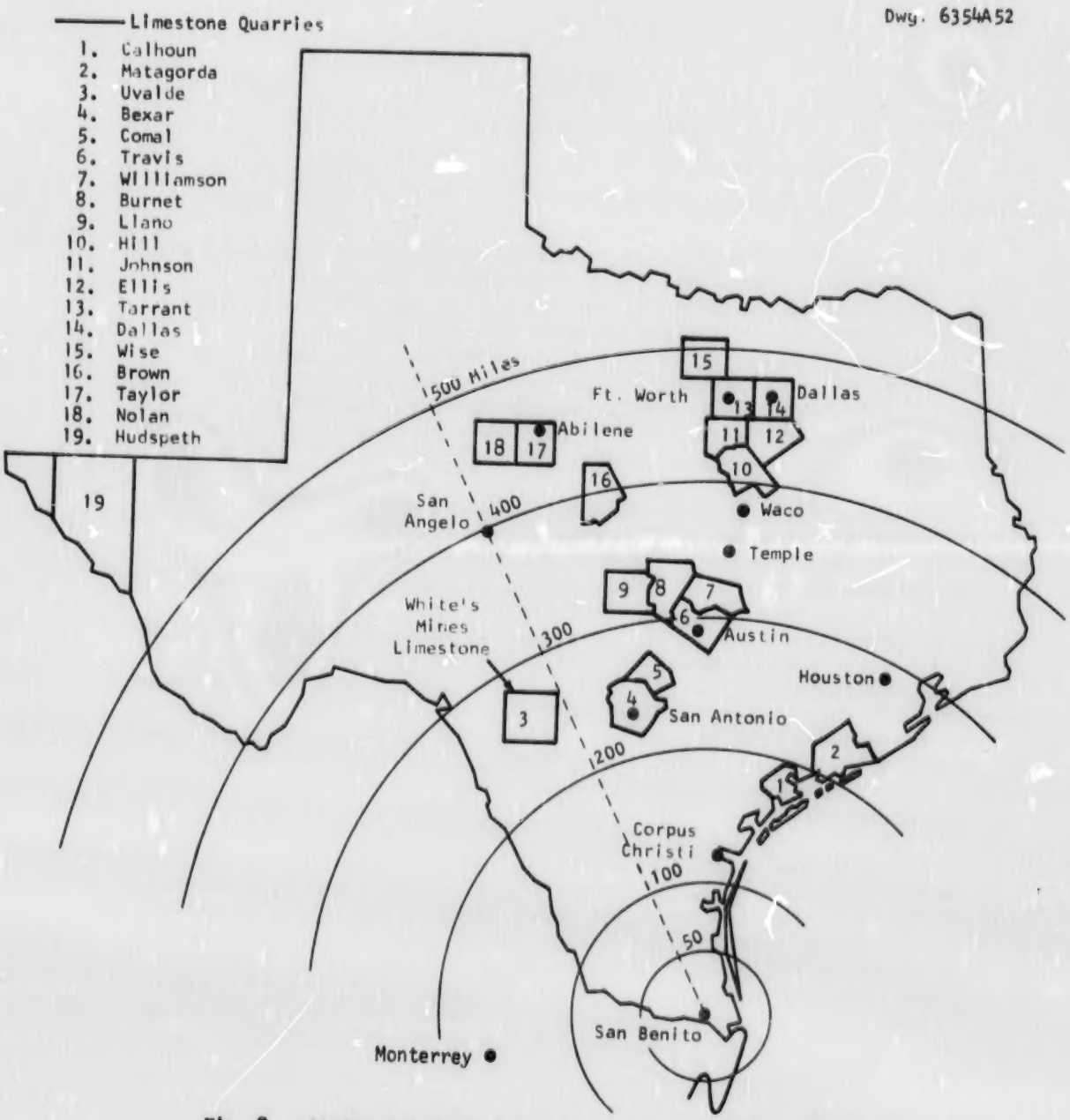

Fig. 2 —Major limestone producing counties of Texas

impurities of Fe_2O_3, Al_2O_3, SiO_2, S and MgO. Analyses of limestone located in the state of Jalisco (Fig. 3) indicated that the material was of high purity which could be adapted for almost any industrial use, and which could be obtained in large quantities. The typical calcium carbonate content range is from 96.93% to 98.64% with silicon present as SiO_2 at 1.14% and 3.4% levels. Limestone which contains < 90% $CaCO_3$, considered as an impure stone, locally outcrops within deposit formations. Detailed chemical analysis of the limestone quarried in Mexico is not obtainable.

In a review of the available literature concerning the quality and location of Mexican limestone the following items should be considered as determinants for potential limestone supplying sites:

1. Limestone obtained from coastal states is chiefly unconsolidated clay material.

2. Large limestone deposits outcrop within central Mexico, principally in the states of Nuevo Leon, Hidalgo, Mexico and Jalisco. (Plants located in the state of Nuevo Leon, at Monterrey and Hidalgo City) are geographically favorable for the transportation of limestone to San Benito, Texas. The distance from the Mexican deposits to San Benito is estimated at 160 to 175 miles. The closest Texas quarry, located in Calhoun County, is approximately 180 miles from San Benito.

3. A high quality marble deposit is located in Vezarron de Montes, bordering the states of Quenrataro and Hidalgo.

LIMESTONE COST

The (late 1975) cost of 3"-5" Texas limestone is $2.00/ton F.O.B. (excluding freight and shipping costs). An additional $2.50-3.00/ton depending on location has been reported for freight expenditures. High calcium limestone, however, can be obtained from producers which quarry in the southern counties of the Edwards Plateau (Uvalde Co., Bexar Co.) and southeastern Balcones Escarpment, located in a 300 mile proximity from San Benito, Texas.

Cost of the material from Mexico, dependent on the initial $CaCO_3$ content, varies from $9.95/ton ($1.25 US/ton) for low-grade material to $19.60/ton ($2.45 US/ton) for high-purity limestone in 1968. The production of limestone is assessed with a tax of $0.45/ton (≈ $0.06 US/ton), and $6.90/ton ($0.85 US/ton) when the stone is of ornamental or marble quality. Due to the decrease in foreign trade, exportation of the material as either natural or crushed stone carries an additional tax of $27.54/ton (≈ $3.45 US/ton). (Price listings for 1968).

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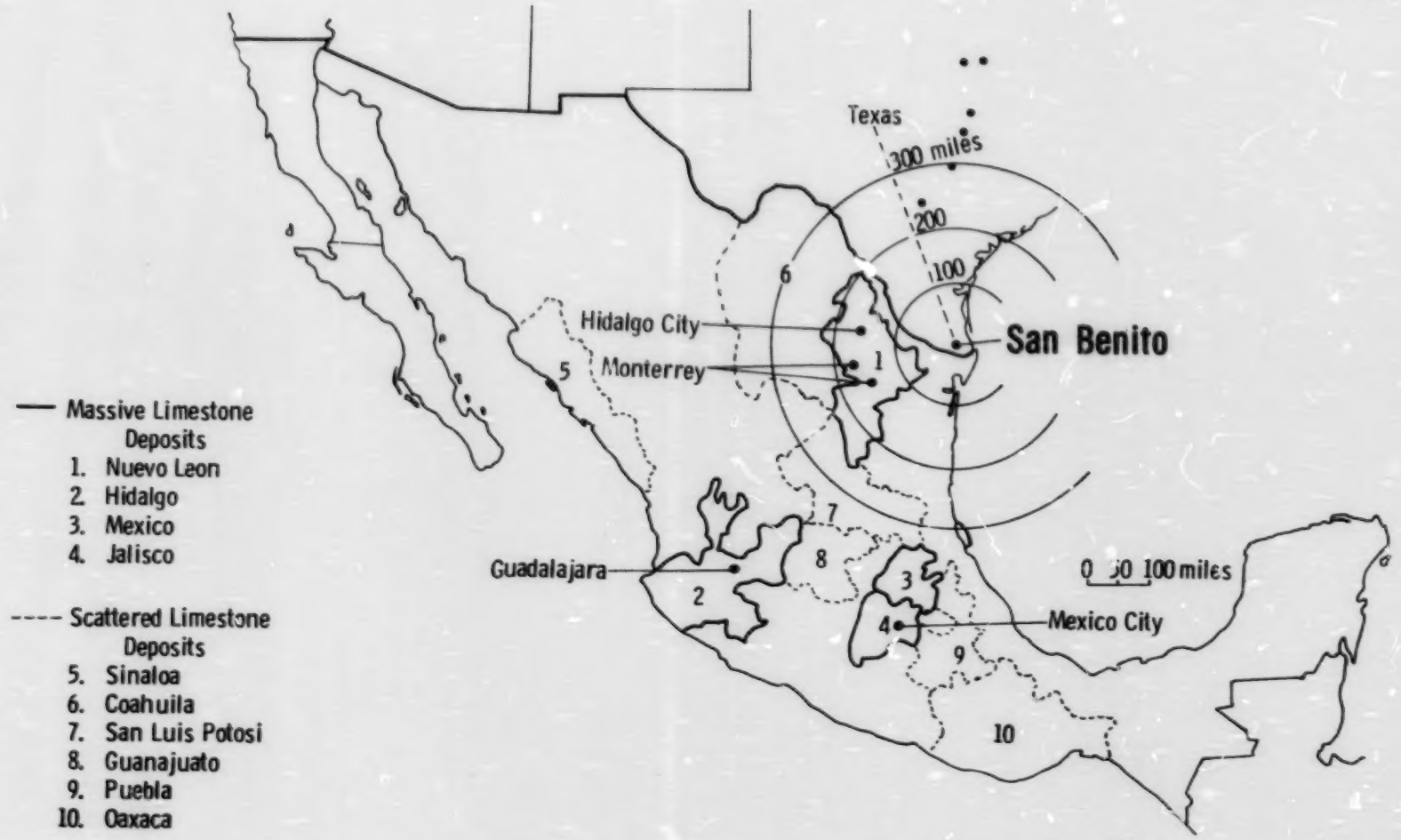


— Massive Limestone Deposits
1. Nuevo Leon
2. Hidalgo
3. Mexico
4. Jalisco

---- Scattered Limestone Deposits
5. Sinaloa
6. Coahuila
7. San Luis Potosi
8. Guanajuato
9. Puebla
10. Oaxaca

Fig. 3 – Major limestone deposits of Mexico

STONES SELECTED FOR TEST PROGRAM

The objective of the test program was to obtain and test samples from each of the areas identified as possible sources of supply for San Benito.

1. No stone samples were received from active quarries in Calhoun or Matagordo counties: one listed operator indicated that their quarry was no longer active.

2. Samples were received from Bexar, Comal, and Burnet Counties (∿ 300 miles from San Benito).

3. Samples were received from Dallas Co. (450 miles from San Benito).

4. A sample was received through Central Power and Light Company. This sample was provided by White Mines - from their Uvalde Co. site (∿ 275 miles from San Benito).

SECTION 6

LIMESTONE SELECTION TEST PROGRAM

CHEMICAL ANALYSES

The analyses of the samples received are listed in Tables 1 and 2. With the exception of the Burnet Stone which was a typical dolomite, all the samples received were high calcium limestones ranging from 92.5% $CaCO_3$ to 96% $CaCO_3$. The residual major impurity was silica, with some alumina silicates. No major trace-element impurities were found by emission spectroscopy, which yields semi-quantitative estimates of environmentally important metals such as lead, beryllium and vanadium.

PHYSICAL CHARACTERIZATION

Stone samples were mounted and polished for examination in the optical microscope. None of the samples had massive-grained structures typical of those which suffer excessive attrition on calcination. The structure of the CP&L stone is shown in Figure 4 and it contains a fairly wide spectrum of grain sizes. The wide distribution of grain sizes seen in Denbighshire limestone is also shown for comparison.

ATTRITION TESTS

The extent to which the limestones were elutriated from a small fluidized bed unit, when calcined in a flow of nitrogen, was measured under standard conditions to obtain a relative attrition index of the stones.[2]

A fifty gram sample of the limestone, 1000-420 microns, was placed in a 3 cm diameter Inconel 800 fluidized bed and heated to 850°C in a flow of nitrogen corresponding to a superficial velocity of 70 cm/sec. The heating rate is linear until the rate of endothermic calcination imposes an additional burden on the electrical heaters. Calcination is essentially complete by the time the sample reaches 830°C.

A Whatman #42 filter in the exhaust line traps fine particles elutriated from the bed. After the experiment excess air is blown down the exit lines to collect any particles which lodge on the tubing walls.

TABLE 1

ANALYSIS OF TRACE IMPURITIES OF TEXAS AND MEXICAN LIMESTONES BY ATOMIC EMISSION SPECTROSCOPY. VALUES REPORTED AS WEIGHT PERCENTS. The Ca and Mg Were Determined By E.D.T.A. Titration

Element	General Portland Cement Company Dallas County	Parker Bros. Comal County	McDonough Bros. Bexar County
Al	.04	.02	.01
Ag	<0.0004	<0.0004	<0.0004
B	<0.0004	<0.004	<0.004
Ba	<0.004	<0.004	<0.004
Be	<0.0004	<0.0004	<0.0004
Bi	<0.0004	<0.004	<0.004
Ca	37.5%	37.0%	38.4%
Cd	<0.04	<0.04	<0.04
Co	<0.0004	0.004	0.004
Cr	0.0004	<0.0004	<0.0004
Cu	<0.0004	<0.0004	<0.0004
Fe	0.3	0.1	0.08
K	0.04	0.004	0.002
Li	<0.0004	<0.0004	<0.0004
Mg			
Mn	0.02	0.008	0.003
Mo	<0.0004	<0.004	<0.004
Na	0.008	0.004	0.004
Nb	<0.004	<0.04	<0.04
Ni	<0.0004	<0.0004	<0.0004
P	<0.04	<0.004	<0.004
Pb	<0.004	<0.0004	<0.0004
Sb	<0.004	<0.04	<0.04
Si	0.8	>10%	~4%
Sn	<0.004	<0.0004	<0.0004
Sr	0.12	0.02	0.02
Ti	0.02	0.0004	0.0004
V	0.0004	0.0008	0.0008
Zn	<0.004	<0.004	<0.004
Zr	<0.004	<0.004	<0.004
Approximate distance from San Benito, Texas:	460 miles	250 miles	235 miles

TABLE 1 (Con't)

Element	Stone: Lone Star Ind., Inc. Burnet County	CP&L Stone (White Mines) (Uvalde)	Materiales Monterrey, Limestone	Frituradas Neuvo Leon Marble	Minera del Norte Monterrey, Neuvo Leon
Al	0.8	0.4	0.03	0.008	0.03
Ag	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
B	<0.0004	<0.004	<0.004	<0.004	<0.004
Ba	<0.004	<0.0004	<0.004	<0.004	<0.004
Be	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Bi	0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Ca	>10%	37.6%	>10%	>10%	>10%
Cd	<0.004	<0.04	<0.004	<0.004	<0.004
Co	<0.004	<0.0004	0.004	0.004	0.004
Cr	<0.0004	<0.004	<0.0004	<0.0004	<0.0004
Cu	<0.0004	0.008	<0.0004	<0.0004	0.008
Fe	0.1	0.2	0.08	0.04	0.09
K	0.2	0.1	0.002	0.0004	0.0008
Li	0.0008	<0.0004	<0.0004	0.0004	<0.0004
Mg	11.8%	≥1%	0.3	0.3	0.3
Mn	0.004	0.04	0.008	0.004	0.035
Mo	<0.0004	<0.004	<0.0004	<0.0004	<0.0004
Na	0.008	0.02	0.0004	0.0004	0.0004
Nb	<0.004	<0.004	<0.004	<0.004	<0.004
Ni	<0.004	<0.004	<0.004	<0.004	<0.004
P	<0.04	<0.004	<0.04	<0.04	<0.04
Pb	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Sb	<0.004	<0.004	<0.004	<0.004	<0.004
Si	0.8	∿2%	∿1%	∿2%	∿1.5%
Sn	<0.0004	<0.004	<0.004	<0.004	<0.004
Sr	0.008	0.08	0.03	0.4	0.03
Ti	<0.004	0.04	0.008	0.002	0.006
V	<0.0004	<0.004	<0.0004	<0.0004	<0.0004
Zn	<0.004	<0.004	<0.004	<0.004	<0.004
Zr	<0.004	<0.004	<0.004	<0.004	<0.004
Approximate distance from San Benito, Texas:	320 miles	255 miles	160 miles	160 miles	160 miles

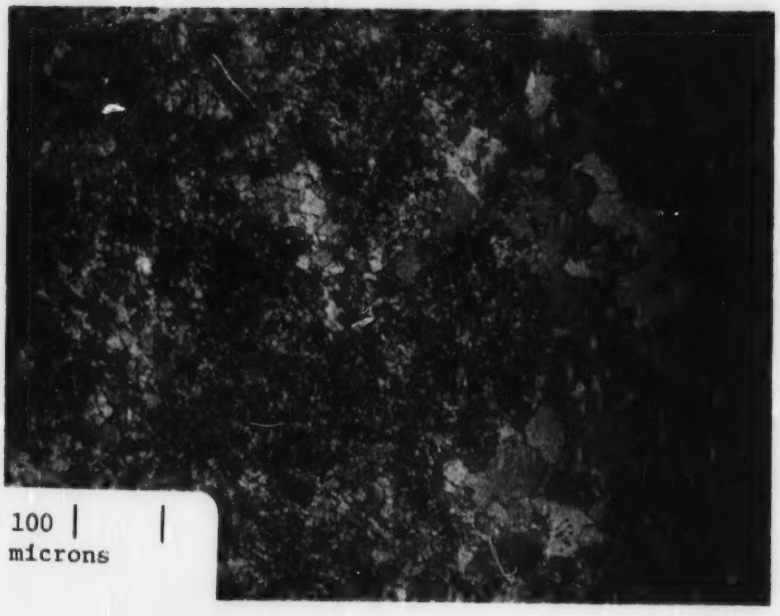
TABLE 2

ANALYSIS OF THE ALKALI DISTRIBUTION IN TEXAS LIMESTONES

	General Portland Cement Co.	Texas Crushed Stone Co.	Parker Bros.	McDonough Bros.
Sodium				
Carbonate	58 ppm	45 ppm	32 ppm	21 ppm
Non-Carbonate	16 ppm	10 ppm	12 ppm	8 ppm
Potassium				
Carbonate	221 ppm	151 ppm	28 ppm	25 ppm
Non-Carbonate	372 ppm	127 ppm	59 ppm	33 ppm

	Lone Star Ind. Inc.	White's Mines, Inc.
Sodium		
Carbonate	160 ppm	72 ppm
Non-Carbonate	13 ppm	66 ppm
Potassium		
Carbonate	120 ppm	148 ppm
Non-Carbonate	1780 ppm	1010 ppm

Denbighshire Limestone



CP and L Limestone (Texas)

FIGURE 4 - The Grain Structure of Sorbent Limestones

The total weight of solids collected gives an indication of the extent of attrition suffered by the stone tested.

Six of the stone samples were tested. One of the stones, from McDonough Co. lost 8.05% of the initial bed weight by elutriation; the remaining five stones lost less than 2.3% in similar tests. The McDonough stone was rejected for further testing. The attrition test results are summarized in Table 3.

CHEMICAL REACTIVITY AS SULFUR SORBENTS

The five remaining stones were tested for sulfur sorption activity by calcining 20 mg samples of a 16/18 mesh sized sample (1200/1000 microns), and reacting the calcine at 871°C with a hydrogen sulfide/fuel gas mixture, in a modified duPont thermogravimetric apparatus, as previously described.

All of the stones tested were extremely reactive, forming 30 molar percent calcium sulfide within eight minutes of exposure to the reactant gas. The stones are therefore indistinguishable in this regard.

The results of the tests carried out are summarized in Table 3.

TABLE 3

PHYSICAL AND CHEMICAL CHARACTERISTICS OF CANDIDATE SORBENTS AND THEIR ATTRITION LOSS ON CALCINATION IN A FLUIDIZED BED

Supplier and Estimated Distance From San Benito In Miles	Type of Stone and Typical Grain Size	Wt % Ca	Wt % Mg	Ignition Loss wt/%	Attrition Loss wt %	Reactivity Time to 30% CaS (Minutes)	Comment
McDonough (San Antonio) 230	Limestone Fine grained (< 20 micron)	38.4		44.2	8.05	- - -	High attrition with finegrained stone-reject
General Portland (Dallas) 460	Limestone Fine grained (∿ 30 micron)	37.5		43.2	2.23	6.7	Acceptable
Parker Bros. (Houston) 220	Limestone (∿ 20 micron grains with 100 micron inserts)	37.0		41.4	1.92	7.5	Acceptable
Burnett (Houston) 320	Dolomite	21.3	11.8	- -	- -	- - -	Not tested
White's Mines, Inc. Stone (San Antonio) 255	Limestone (4-30 micron)	37.6		42.1 42.6	1.04	7.6	Very low attrition looks promising, as a candiate stone
Minera Del Norte 160	Limestone (< 16 micron)	38.5	0.50	- -	0.6	7.5	Acceptable
Monterrey 160	Limestone (30-200 micron)	38.2	0.85	43.3	0.4	11.1	Possible

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APPENDIX

TEXAS LIMESTONE PRODUCERS

Dwg 25/C274

Company	Address	County	Contact	Comment
Austin White Lime, Co.	McNeil, Texas 78651	Travis	Mr. Jerry Hurta (512-255-3646)	– Two operational quarry sites located north of the McNeill plant – Third quarry two miles east of McNeill – Chemical analysis shows high quality limestone - $CaCO_3$ varies from 97% - 99.5% CaO averages 55%, negligible magnesium present – Floor of first 30' level contains massive chert beds, followed by dolomite deposits
McDonough Bros., Inc.	Fredericksburg Rd. Route 8, Box 222 San Antonio, Texas 78228	Bexar	Mr. Kerner (512-696-8500)	– Production began in 1968 – Operations of two large quarry sites along IH10 one mile north of FM1604 and 15 miles north of San Antonio. Lime plant is located east of the quarry area – Quarry is located in the fault zone complex of the Balcones – Mainly quarry Edwards limestone – Chemical composition - average $CaCO_3$ ~ 99% – Layers of chert nodules – Produces agricultural limestone, chemical and industrial stone
Round Rock Lime Co.	P.O. Box 218 Round Rock, Texas 78664	Hill Williamson	(512-255-3611)	– Hill county quarry located 1 mile south of H174, 4 miles west of Blum – Comanche and Edwards Formation - Edwards limestone makes up principle quarry stone - which is a complex fossilized reef - Fossils contain Fe_2O_3 & SiO_2 - and numerous calcite crystal deposits are found within the rocks – Williamson County quarry – 2 non-operating quarry sites - all crushed stone used for kiln feed for both sites is trucked from Snead Quarry at Georgetown – No overburden problem – Numerous interbedded layers of SiO_2 and dolomite/limestone – Moderate fossil content – Numerous cavities and veins dissect quarry face, filled with calcite crystals
Texas Lime Co.	P.O. Box 851 Cleburne, Texas 76031	Johnson	(817-645-6680)	– Two operational plants, in 1968 only one plant was in use - produces hydrate and quicklime - shipment by truck or rail – The city plant is located 12 miles west of Cleburne - major production is agricultural lime, fillers, chemical and industrial process stone – Cleburne (West) Plant - located 12 miles west of Cleburne on Park Road 21, Johnson County began in 1961. Quarry face is approximately 35 feet high belonging to the Edwards limestone formation – Minor stripping is needed to remove the overburden of 2-5' of Kiamichi and Marl – Quarry floor is composed of impure limestone from the Comanche peak formation
U. S. Gypsum Co.	101 South Wacker Dr. Chicago, Illinois 60606	Comal Harris		– Location 2 miles southwest of Braunfels – Shipment by rail or truck – 20 feet overburden (maximum overburden is 60') – 35' section of 'purity' limestone
Whitestone Lime Co.	Cedar Park, Texas	Williamson		– Plant and quarry are located 1 mile southwest of Cedar Park on FM1431 – Mainly quarries Walnut Formation; little Comanche Peak & Edwards – 5-6 feet overburden – Average $CaCO_3$ content is 98% - 99%

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Company	Address	County	Contact	Comment
Barrett Industries	2718 S.W. Military Drive Box 21070 San Antonio, Texas 78221	Bexar	(512-661-6550)	– No longer active mining
General Portland Cement Co.	2800 Republic Bank Tower Dallas, Texas 75201	Dallas Tarrant	Mr. W. Alderete (214-233-6865)	– Limestone quarried in Dallas County is mainly an Austin Chalk – Limestone quarried in Tarrant County is a soft, sedimentary stone – Typical chemical composition - 51.0% CaO, 1.0% MgO, 5.0% SiO_2, 0.5% Al_2O_3, 0.5% Fe_2O_3, 0.02% Mn_2O_3, 0.05% Na_2O, 0.15% K_2O, LOI 42.0%
Gifford-Hill & Co., Inc.	P.O. Box 47127	Wise	Mr. J.R. Jones (214-637-3860) (214-827-7720)	– Typical chemical composition - 96.46% $CaCO_3$, 0.71% $MgCO_3$, 1.09% SiO_2, 1.30% Al_2O_3, 0.19% Fe_2O_3 – Numerous interbedded layers of Dolomitic limestone
Lone Star Industries, Inc.	P.O. Box 47327 Dallas, Texas 75247	Burnet Nolan Calhoun Ellis Wise Hudspeth	Mr. W.R. Womack (214-631-8640)	– Typical chemical composition - 53.14% CaO, 0.64% MgO, 3.49% SiO_2, 0.36% Al_2O_3, 0.40% Fe_2O_3, LOI 41.86%
Parker Bros. & Co., Inc.	P.O. Box 107 Houston, Texas 77001	Comal Matagorda	Mr. W.D. Bankston (713-637-2222)	– Main quarry is located northeast of San Antonio – High purity stone (95-98% $CaCO_3$ – SiO_2 is usually less than 1%
Texas Crushed Stone Co.	P.O. Box 9345 Austin, Texas 78717	Llano Williamson	Mr. Dale Bryan (512-863-5511)	– Dolomitic limestone
Texas Industries, Inc.	P.O. Box 140 Midlothian, Texas 76065	Ellis Wise	Mr. John Radney (214-775-3449)	
Trinity Concrete Products	P.O. Box 47524 Dallas, Texas 75247	Johnson Wise	Mr. Ned Finney (214-638-4700)	– Limestone quarried in Wise County is from the Pennsylvanian Age – 98-99% $CaCO_3$ – Hill County quarries are Lower Cretaceous Formations – CaO content averages ~ 43% – Interbedded Al_2O_3 viens – Pure Dolomite formations – Excellant outcrop region is in the Edwards Reef Complex Formation in the Curshberg Lagoon – Approximately 100 miles in diameter – West of Interstate 35, south of Interstate 20 and northeast of Interstate 10
White Mine's, Inc.	P.O. Box 500 Brownwood, Texas 76801	Brown, Uvalde, Taylor	(915-646-8526)	